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DILUTE ACID PRETREATMENT OF BIOMASS

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ABSTRACT

A preliminary process design for dilute acid pretreatment of aspen wood chips has been prepared and subjected to an economic evaluation. The process design was prepared according to experimental data on the kinetics of dilute acid prehydrolysis and particle size effects obtained in this study. The initial economic evaluation shows that the production costs for the fermentable sugar products are primarily governed by feedstock costs while capital investment and energy costs are less important. The predominant capital cost is associated with an expensive acid resistant pretreatment reactor, while a large fraction of the total electrical energy is needed for dry milling of aspen chips to small (20-80 mesh) particles needed for rapid acid penetration and enzymatic saccharification. The results indicate that improvements in the process design will require development of a cheaper pretreatment reactor and a less energy intensive comminution system. We have also completed initial investigations of the conditions for complete removal of lignin from acid treated aspen wood meal and wheat straw with dilute (1 to 4%) aqueous solutions of sodium hydroxide in the temperature range of 100 - 160°C. The alkaline delignifications produce highly digestible cellulosic substrates but are in most cases accompanied by significant losses of cellulose. Dilute acid pretreatment of aspen bark has also been recently initiated.

DILUTE ACID PRETREATMENT OF BIOMASS

INTRODUCTION

Prehydrolysis of aspen wood and wheat straw meals with dilute sulfuric acid at moderate (120-160°C) and high (180-230°C) temperatures has been shown to be an effective pretreatment for increasing the digestibility of cellulose by a cellulase enzyme complex produced by mutants of the fungus Trichoderma reesei (Grohmann et al 1984, 1985, 1986, Himmel et al 1985, Torget, 1985, Torget et al, 1987, Grethlein 1980, 1985, Grethlein et al, 1984, Knappert et al, 1980, 1981, Allen et al, 1983, Sudo et al, 1986). The past experimental work performed at SERI led to the following important observations:

1. The increase in enzymatic digestibility of cellulose in pretreated wheat straw and aspen wood correlates strongly with hydrolysis of hemicelluloses in both substrates during acid catalyzed pretreatment (Grohmann et al, 1985).
2. ~~The power consumption for dry milling of wheat straw and aspen wood to~~ relatively coarse meals (+100 mesh to -1/2 inch) is not prohibitively high and costly. A less complete set of data was also obtained for corn cobs and corn stover, two major agricultural residues (Himmel et al, 1985).
3. The agricultural residues are much more friable than aspen wood therefore their milling consumes much less energy (Himmel et al, 1985).
4. Knife mill is more efficient equipment for milling of wheat straw, corn stover and aspen wood than a hammer mill is, but the knife mill is also very sensitive to mechanically tough fractions in some biomass (corn cobs) and contaminants (eg. metals and stones) introduced with biomass feedstocks.
5. The dilute acid pretreatment can be readily extended to operation at high concentrations (i.e., up to 40 wt%) of solids (Grohmann et al, 1986). The operation at high concentration of solids will lead to sizable savings in the consumption of steam and in the case of aspen wood. An additional saving in the amount of acid catalyst would be realized. The savings in the consumption of acid catalyst are much smaller for wheat straw because the relatively high ash content neutralizes some of the catalyst.
6. Preliminary process design and economic evaluation of the dilute acid pretreatment was prepared for aspen wood. The results indicated that dilute acid pretreatment can provide feedstock for enzymatic saccharification at competitive costs when compared to other pretreatment options under development (Torget et al, 1987).
7. Addition of surfactants to dilute sulfuric acid increases the effectiveness of the pretreatment of wheat straw only to a small extent (Grohmann et al, 1984, and Torget, 1985).

We have also confirmed sporadic previous observations that the hydrolysis of hemicelluloses (xylans) is biphasic in hardwoods and obtained evidence that it is biphasic in wheat straw (Torget, 1985, Grohmann et al, 1985). The rate of hydrolysis of xylan backbones can be best described as two concurrent reactions, one fast and one slow. Approximately 70% of the xylan backbone in aspen wood hydrolyzes via a fast reaction and 30% via a slow reaction regardless of temperature in the range of 95°-140°C. The behavior of the xylan in the wheat straw seems to be different from that in aspen wood, because the fraction of xylan which hydrolyzes slowly decreases as the temperature of the pretreatment is increased from 95° to 140°C. The biphasic rate of xylan removal has significant implications for the pretreatment and xylose yields. The effective pretreatment requires nearly complete removal of xylan, which proceeds rapidly only at 120°C or above with low (c.a. 0.5%) concentrations of sulfuric acid we have been investigating. The presence of a slow fraction also decreases the xylose yield in some process configurations because more xylose is converted to furfural while the slow fraction is being hydrolyzed. Nevertheless, the xylose is produced in approximately 80% yield during dilute acid pretreatment of both substrates.

Independent investigations by H. Grethlein and coworkers (Grethlein, 1980, 1985, Grethlein et al, 1984, Knappert et al, 1980, 1981, Allen et al, 1983) which were performed at higher temperatures (180° - 230°C) provide additional information that the pretreatment is effective for mixed southern hardwoods but not for softwoods (pine). They also made a very important observation (Grethlein, 1985), that dilute acid pretreatment creates pores in the wood which are large enough for enzyme molecules to penetrate and access cellulose fibers. The large pores are probably produced by removal of hemicelluloses and concurrent condensation of lignin.

The investigations in FY1987 were concentrated on issues important for the process design and evaluation, namely particle size effects on both dilute acid pretreatment and subsequent enzymatic saccharification, determination of knife mill throughput as the function of particle size, and determination of bulk packing density of aspen wood at various particle sizes. Process design and economic evaluation of dilute acid pretreatment were performed for aspen wood chips (Torget et al, 1987).

The experimental work was also concentrated on studies of alkaline delignification of acid treated wheat straw and aspen wood. The dilute acid pretreatment of aspen bark has been initiated as well.

Materials and Methods

Substrates and Other Materials. Air-dried, debarked aspen logs were coarsely chipped, milled in knife mills, and wood particles screened to various particle size fractions. The air-dried baled wheat straw was shredded in a garden shredder, then knife milled and screened. The aspen bark was obtained manually from harvested dormant aspen trees using a draw knife. It was air dried, milled, and screened in the same fashion as aspen wood.

A cellulase preparation (Celluclast 1.5L) produced by Trichoderma reesei was a gift of NOVO Industries, Ltd. (Copenhagen, Denmark). The cellulase preparation was in liquid form, stabilized by the addition of glycerol. The

specific activity of the enzyme preparation was approximately 72 International Filter Paper Units (IFPU)/ml (Ghose, 1987). Fungal β -glucosidase (Novozyme 188; NOVO Ltd., specific activity 250 I.U./ml) was used to supplement the β -glucosidase activity in the cellulase preparation. The remaining chemicals were purchased from national laboratory supply houses.

Chemical Pretreatments and Analysis. The aspen wood, aspen bark and wheat straw particles were pretreated with dilute (0.45-0.5%) sulfuric acid and dilute (1-4%) sodium hydroxide solutions in a 1 quart or 2 gallon stainless steel reactors (Carpenter 20 Cb-3, Parr Co., Moline, Illinois) equipped with impeller mixers and pressurized injection device (Himmel et al, 1986). Due to mixing limitations of impeller mixer with biomass particles, only low (5-10%) solids slurries were investigated. Dilute acid pretreatment experiments were performed at 140 and 160°C while alkaline delignification experiments were performed in the temperature range of 100-175°C. Reaction times are specified in the text and start when the slurries of biomass in deionized water reach the desired reaction temperature and acid or base is injected. A large part of alkaline delignification experiments was also performed with wheat straw and aspen wood pretreated with dilute sulfuric acid at 10% concentration of solids in 50 gal. glass lined Pfaudler reactor. Since rapid temperature changes are impossible to achieve in this large reactor the approximate reaction conditions were as follows: heat up time, 1 hour; reaction time at 140°C, 1 hour; and cool down time, 1 hour. All pretreated biomass particles were exhaustively washed with distilled water to allow removal of hydrolyzed water soluble components.

Lignin and other acid insoluble components (e.g. silica) were determined as Klason lignin (Moore and Johnson, 1967). Carbohydrate composition of solids was determined by modified two-stage sulfuric acid hydrolysis (Moore and Johnson, 1967, Grohmann et al, 1984). Monosaccharides in neutralized hydrolyzates were determined by ion-moderated partition chromatography on Bio-Rad (Richmond, CA) cation exchange columns in Pb^{2+} and Ca^{2+} forms using refractive index detection.

Enzymatic hydrolysis was performed in batch mode at 45°C in gently rotated glass vials. Cellulase enzyme loading was approximately 42 I.F.P.U./gm of cellulose (β -glucosidase activity was approximately 25 I.U./gm of cellulose) and initial cellulose concentrations were adjusted to approximately 1%. Glass beads used for shearing action of the wood particles were not present in the enzymatic digestion studies unless stated. The reaction times are specified in the text. Glucose released by the enzymatic hydrolysis was determined with an YSI glucose Analyzer (Yellow Springs Instruments, Yellow Springs, OH) and by ion moderated partition chromatography when information about other sugars was required.

Process Engineering Design Assumptions and Calculations. The feed material to the plant was assumed to be commercial 1-inch aspen wood chips containing 50% moisture content and having the chemical composition described previously (Grohmann et al, 1985, 1986). The size of the pretreatment facility was based on a base case of producing 25 million gallons of absolute ethanol from the total potentially fermentable hexose and pentose streams produced from the pretreatment. The location of the plant was arbitrarily chosen as the southeastern United States for two reasons: there is a surplus

of underutilized hard wood in that region of the country; and the weather is relatively mild year around, thus allowing the delivery of wood chips on a continuous basis and requiring a relatively inexpensive wood receiving and handling yard. The yield of hexoses was assumed to be 100%, whereas the pentoses were assumed to undergo 20% thermal destruction during the pretreatment. Although use of 100% of the hexose available in the feedstock for the calculation of yield of ethanol produced by the plant is admittedly very optimistic, this remains the goal of our research efforts. The overall recovery of sugars from the prehydrolysis was calculated at 98.6%. The fermentation yield of ethanol from sugars was 95% of theoretical, while the ethanol recovery yield was calculated at 99.5%.

A wood receiving and handling facility, a comminution step, and a dilute sulfuric acid pretreatment process were designed in detail from our research data and the best currently available information (Grohmann et al, 1985, 1986, Torget et al, 1987, Arthur D. Little, 1985, Badger Engineers, Inc., 1984, Chem Systems, Inc., 1983, Iotech Corp., 1982, Stone and Webster, 1985, Wilke et al, 1985). To estimate capital costs in a consistent manner, the ICARUS computer-aided cost estimating program was used. This program produces a detailed time and materials estimate with an accuracy of $\pm 10\%$ for a completely defined process (ICARUS, 1984). Vendor quotes for specific unique process equipment items were used whenever possible and supplied to the ICARUS program to assure quality of the estimate.

The costs of the feedstock, chemicals, process water, electricity, and steam were obtained from vendor quotes, SERI studies (Wright et al, 1986), and the Chemical Marketing Reporter. The energy balances were calculated assuming the feed chips, process water and acid to be at 60°F. The enthalpy of the low pressure steam was obtained from steam tables, and the specific heat of bone dry aspen wood was assumed to be 0.32 BTU/lb. The capital charges were calculated using a fixed charge rate (FCR) of 0.13 times the inside battery limits (ISBL) (Argonne National Laboratory, 1985).

RESULTS AND DISCUSSION

A. Process Design and Economic Evaluation

A.1. Process Design Data. The capital cost as well as the energy cost of the comminution step(s) has a significant impact on dilute acid and many other pretreatment processes. Therefore, we have investigated the effects of size of the aspen wood chips as it relates to the rates of both enzymatic saccharification and xylan hydrolysis.

The enzymatic digestibility of cellulose in screened aspen particles pretreated with dilute acid to remove greater than 90% of the xylan [140°C, 60 min, 0.5% H₂SO₄ (v/v), 10% solids] was investigated first. All pretreated screened particles were chemically analyzed for xylan content. The xylan removal was found to average between 91% and 96% of the starting xylan in untreated wood. The results for long-term digestibility of cellulose in uniformly pretreated aspen wood particles are shown in Table 1. The experimental protocol used two approaches. In the first system, the wood particles

TABLE 1.

ENZYMATIC DIGESTIBILITY OF THE CELLULOSE IN ASPEN WOOD SOLID RESIDUES
AFTER ACID PRETREATMENT AT 140°C FOR ONE HOUR AS A FUNCTION OF MESH
SIZE AND SHEARING ACTION DURING THE ENZYMATIC DIGESTION

Mesh Size Range	Weight Percent Anhydroglucose Released from Total Glucan Present in the Pretreated Residues	
	Glass Beads Present in Reaction Vessel	No Glass Beads Present in Reaction Vessel
3/8" - 1/2"	62	52
1/4" - 3/8"	77	76
5 Mesh - 1/4"	84	78
5 - 8	77	77
8 - 12	78	78
12 - 16	84	84
16 - 20	82	82
20 - 35	76	76
35 - 60	81	81
60 - 80	79	79
Alpha - Cellulose Control	95	94

TABLE 3.

CAPITAL COST AND ENERGY CONSUMPTION OF THE MAJOR SECTIONS
OF PROCESS EQUIPMENT FOR PRETREATMENT

Equipment	Installed Capital Investment (\$ Millions)	Electricity (KWH x 10 ⁻⁶)	Steam (lb _m x 10 ⁻⁶)
Wood Handling and Storage	3.69	0.9	0
Knife Mill	0.65	27.1	0
Prehydrolysis Reactor	4.01	1.1	229
Blowdown Tank and Neutralization Mixer	1.10	0.3	0
Conveyors, Pumps, Storage Tanks, and Misc.	<u>1.75</u>	<u>0.1</u>	<u>0</u>
TOTAL	11.20	29.5	229

were gently tumbled in the presence of the cellulase enzyme complex and several glass beads (6 mm in diameter) to simulate mild abrasive action during the digestion process. In the second system, the wood particles were slowly tumbled with enzyme and buffer alone. The results from both systems indicate that a clear drop in digestibility occurs when the particle size of pretreated aspen wood reaches 1/4 - 3/8" size, and the additional grinding action in this system provides slightly higher cellulose digestion.

The results of the kinetic experiments were more revealing (Figure 1). The most rapid digestion was obtained for particles in the 60-80, 40-60 and 40-20 mesh size ranges, and rates became very slow for the particles larger than 5 mesh. Since the enzymatic hydrolysis of cellulose is by far the slowest step in the overall conversion of cellulose in biomass to soluble sugars, the results in Figure 1 show that the optimal particle size of the pretreated aspen wood for enzymatic hydrolysis is approximately 20 mesh or less.

The situation is similar but less severe in the dilute acid pretreatment step. The preliminary data shown in Figures 2 and 3 indicate that the reaction time needed for high (above 90%) removal of xylan is 2-3 times longer for particles in the 1/2 - 1 inch range than for sawdust (20-80 mesh). Since the xylan removal correlates highly with enzymatic digestibility of cellulose in pretreated aspen wood (Grohmann et al, 1985, 1986), the reaction conditions have to be always adjusted to achieve the necessary degree of hydrolysis of xylan.

The problem is compounded by a decrease in bulk packing density of wood as the particle size is increased. Experimental results for aspen wood are shown in Figure 4. The decrease in particle size from the 1/2 - 1 inch range to sawdust (20-80 mesh) allows an approximately 44% increase in bulk packing density of aspen wood in the pretreatment reactor.

The negative effects of large particle size are somewhat offset by a large decrease in electrical power consumption needed for milling of aspen chips to smaller particles (Himmel et al, 1985) and by increased throughput of knife mills (Figure 5) needed for this operation. However, the large pretreated particles would have to be mechanically disintegrated to smaller particles for subsequent enzymatic hydrolysis to increase the rate of cellulose hydrolysis (Figure 1). Since dilute acid pretreatment under conditions (140 - 160°C) we have investigated does not provide sufficient pressure drop for chip disintegration by rapid decompression and since experimental data on comminution of wet, pretreated aspen chips are lacking at the present time, the preliminary process design is based on initial comminution of dry, debarked wood chips and chemical pretreatment of small (approx. 20 mesh) particles.

A.2. Overall Process Description. The simplified flow diagram of the process is shown in Figure 6. Fresh aspen chips are delivered by truck, debarked and cleaned through the shearing action of an auger cleaner (Morbark Industries Inc., Winn, MI), and stored for no longer than one month. The debarker-cleaner is not shown in Figure 6, but is included in the detailed process design as are several other minor pieces of process equipment. Chips are then transferred to a knife mill equipped with a 1/16" screen to produce particles primarily in the 20 to 80 mesh range (Himmel et al, 1985).

TABLE 4.
Substrates for Alkaline Delignifications

Aspen wood or wheat straw pretreated with 0.5% (v/v) sulfuric acid

	Average Composition (wt%)			
	Aspen Wood		Wheat Straw	
	140°/60 min	140°/15 min	140/60 min	140/20 min
Anhydroglucan	67	61	65	61
Anhydroxylan	2	5	3	5
Klason Lignin + Ash	31	29	32	30
Enzymatic Digestibility of Cellulose (96 h)	86%	87%	99%	89%

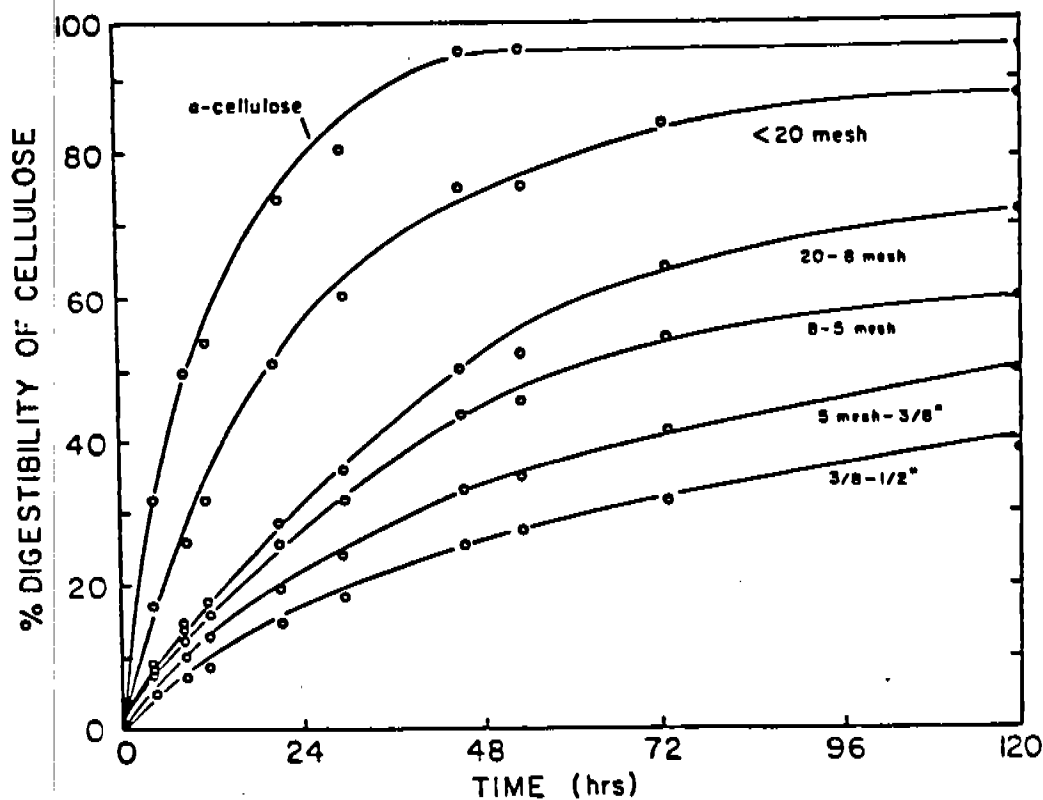


Figure 1. Enzymatic digestibility of cellulose in chemically treated aspen wood (140°C/one hour, 0.5% H_2SO_4 v/v, 10% solids) using NOVO Celluclast 1.5L cellulase supplemented with beta-glucosidase as a function of particle size compared to an α -cellulose control.

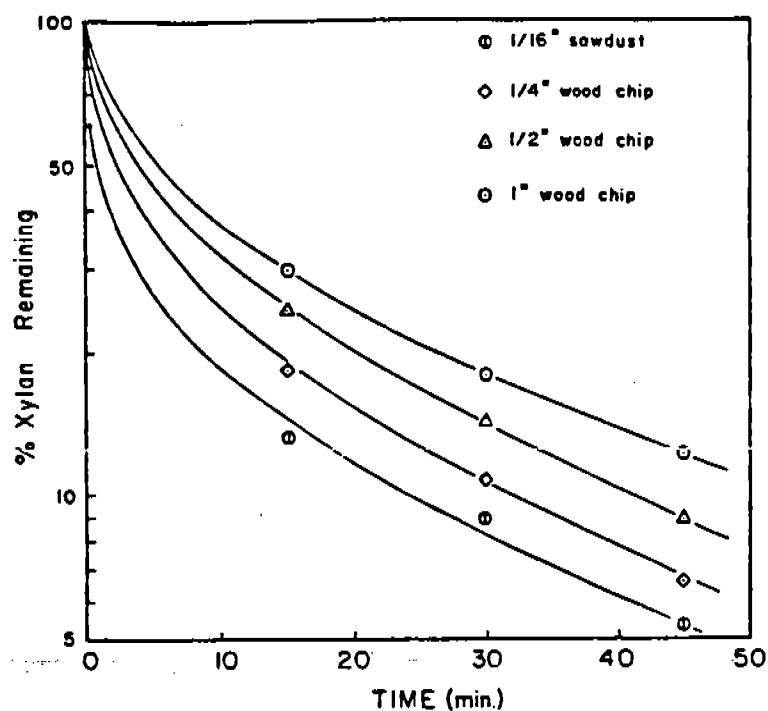


Figure 2. Anhydroxylose remaining in solid residues versus time of dilute acid hydrolysis (0.5% v/v H_2SO_4) of aspen wood (5 wt% solids) at $140^\circ C$ using four different wood chip sizes.

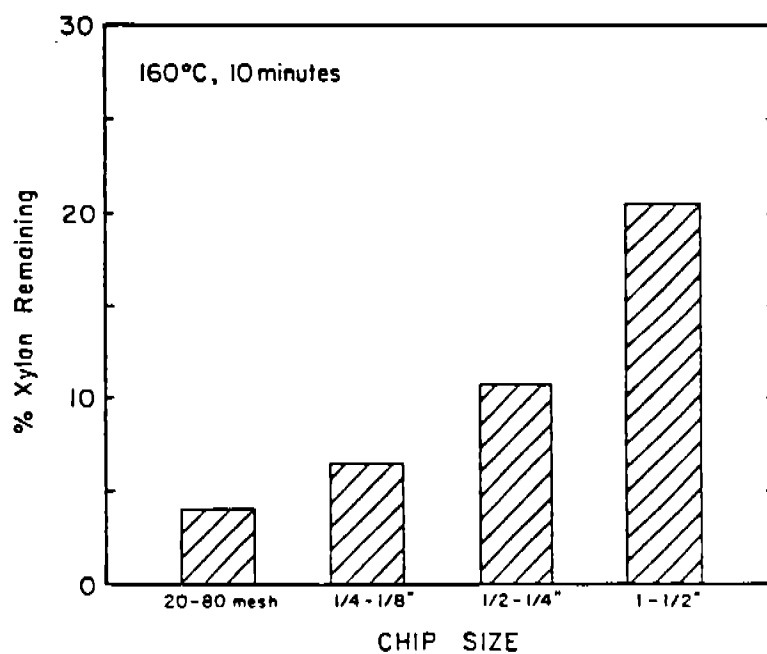


Figure 3. Anhydroxylose remaining in chemically pretreated aspen wood (0.5% H_2SO_4 v/v, $160^\circ C$ /10 min, 5 wt% solids) as a function of particle size.

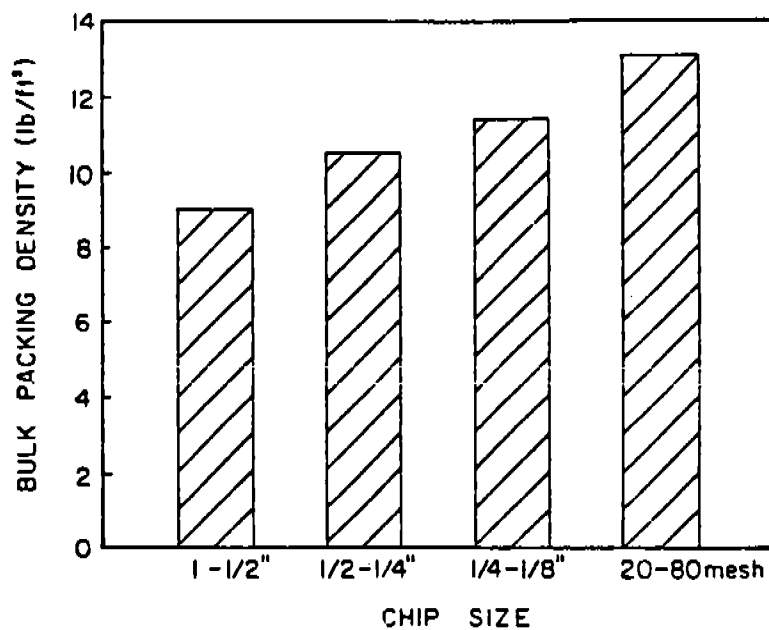


Figure 4. Bulk packing density of oven dried aspen wood (45°C) as a function of chip size.

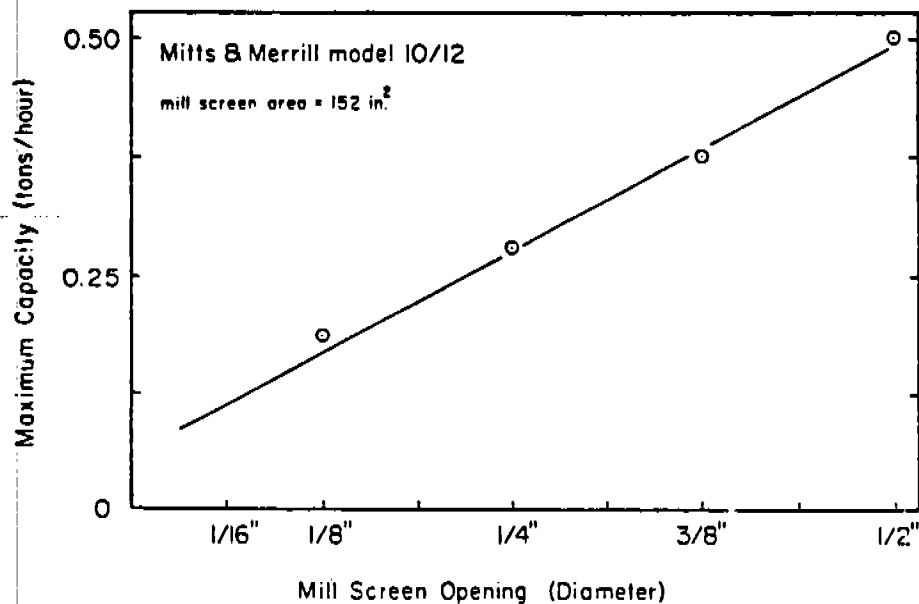
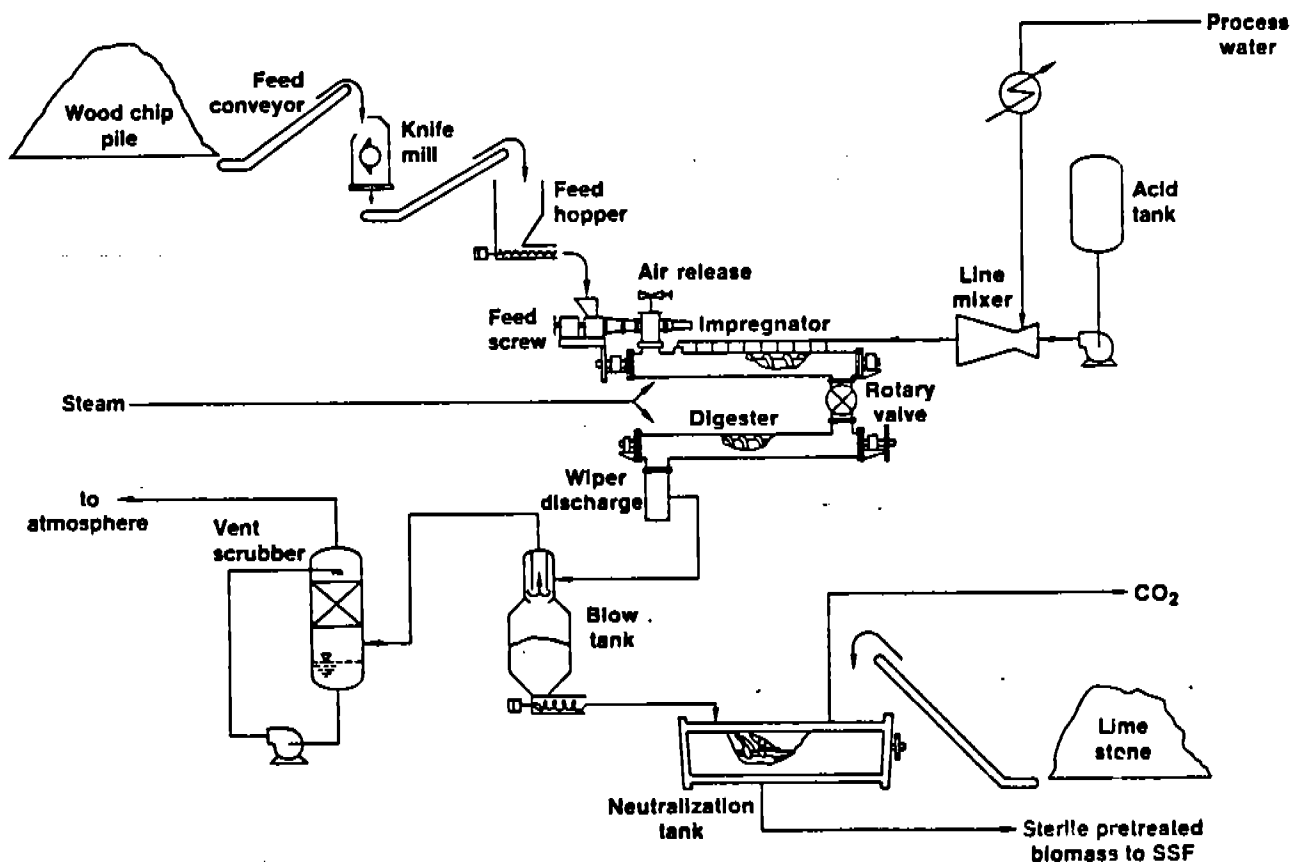


Figure 5. Maximal feed rates of aspen wood chips through a Mitts and Merrill knife mill with a fixed size mill screen (152 in²) as a function of chip size.



Dilute Sulfuric Acid Pretreatment Simplified Schematic

Figure 6. A simplified schematic process flow diagram of a dilute sulfuric acid pretreatment for aspen wood meal.

After milling, the wood particles are fed to a continuous Pandia digester (Shartle-Pandia Division, Middletown, OH) via a feed hopper and pressurized screw feeder. The continuous prehydrolysis is based on Pandia continuous pulping digester which has been used for similar operations in the pulp and paper industry (Markham and Courchene, 1980). All equipment to be in contact with hot, dilute sulfuric acid is assumed to be constructed from Carpenter 20 Cb-3 stainless steel, which exhibits high corrosion resistance under these conditions. The use of much cheaper 316 stainless steel was avoided because in our experience it suffers from high corrosion rates in hot, dilute sulfuric acid.

The continuous digester is composed of two parts connected by a rotary pressure valve. The wood in the first section is impregnated with hot dilute sulfuric acid, preheated by it and also deaerated. The flows of wood, hot dilute sulfuric acid, and additional steam are adjusted for the mixture to reach approximately 95°C at the end of the first section, and residence time of solids in the first section is assumed to be 10 minutes. The impregnated hot wood is then transferred to the second section where it is rapidly heated by steam injection to 160°C. The residence time of solids in this section is also assumed to be 10 minutes to conform with our previous kinetic data (Grohmann et al, 1985, 1986).

The initial concentration of solids in the digester is calculated to be 30 wt%. The concentration of solids at the exit is of course lower since approximately one third of the aspen wood is dissolved in the pretreatment process. The hot pretreated mixture is discharged into a blowdown tank where it is rapidly cooled to 95°C by evaporation of entrained water. Rapid cooling of the pretreated wood will minimize the degradation of xylose to furfural which is detrimental to subsequent saccharification/fermentation steps. The vapors are purified by passage through a vent scrubber to remove small amounts of acetic acid, furfural and other volatile organics produced by the pretreatment process. The hot acidic solids are then transported to the neutralization blender where they are mixed with limestone powder. Carbon dioxide produced by neutralization will be vented to the atmosphere. It should be noted that pretreated solids are kept hot after the pretreatment to preserve their sterility for subsequent saccharification/fermentation.

A.3. Discussion of the Process Design and Economics. This preliminary process design and economic analysis had two major goals. First, a relatively detailed equipment list combined with the overall mass and energy balance was needed to yield a model to begin a parametric study of the key process variables. And second, if the process economics seem encouraging, then areas of uncertainty in the process need to be explored and characterized through further research before pilot studies can be initiated.

The estimated cost of production per pound of total sugar produced by the process is seen in Table 2. The cost of operating the plant (before by-product and steam credits) is approximately 4.50 c/lb of fermentable sugar (C₅ and C₆) or \$0.621/gal ethanol. The major cost is that of the wood feedstock (2.54c/lb, or 56% of the total production cost) with capital charges and utility costs primarily contributing to the remaining cost of production. Thus, the overriding parameters which affect the economics of sugar production from aspen wood chips via dilute acid prehydrolysis are feedstock costs and yield of the sugars produced. The total cost of sugar is somewhat deceiving

TABLE 2.

ESTIMATED COST OF PRODUCTION FOR DILUTE SULFURIC ACID PRETREATMENT

Basis: U.S. Southeast, 1st Quarter 1987
 Capacity: 345 Million lb/yr Potentially Fermentable Sugars (C₅ and C₆)
 Operating: 8,000 h/yr for 25 Million gal/yr Ethanol

CAPITAL COST SUMMARY (\$ 10⁶)

Inside Battery Limits (ISBL)	11.2
Offsites (20% ISBL)	2.2
TOTAL FIXED INVESTMENT (TFI)	13.4
Working Capital (10% of TFI)	1.3
TOTAL UTILIZED INVESTMENT	14.7

PRODUCTION COST SUMMARY

	Units/Yr	Price (\$/Unit)	Annual Cost (\$10 ³)	Ferm. Sugars (C ₅ & C ₆) cents/lb	\$/gal Ethanol
Raw Materials					
Wood Chips-Feedstock, Tons (Dry)	208,800	42.00	8,770	2.54	
Sulfuric Acid, Tons	5,359	65.00	349	0.10	
Calcium Carbonate, Tons	5,468	34.00	186	0.05	
TOTAL RAW MATERIALS COST			9,305	2.69	0.372
Utilities					
Power (KWH)	29,500,000	0.05	1,474		
Process Water (10 ³ gal)	34,900	0.60	21		
Steam, 150 psi, (10 ³ lb)	229,000	4.00	916		
TOTAL UTILITIES COST			2,411	0.70	0.096
Operating Costs					
Operators (3/shift, \$26,000/man)			328		
Supervision			35		
Maintenance Material & Labor (6% of ISBL)			672		
TOTAL OPERATING COSTS			1,035	0.30	0.041
Overhead Expenses					
Direct Overhead (45% Labor + Supervision)			163		
General Plant Overhead (65% Operating Costs)			673		
Insurance, Taxes (1.5% of TFI)			201		
TOTAL OVERHEAD EXPENSES			1,037	0.30	0.041
TOTAL COST OF PRODUCTION			13,788	4.00	0.551
Fixed Charge Rate (0.13)			1,742	0.50	0.070
NET COST OF PRODUCTION			15,530	4.50	0.621

because the pretreatment produces only approximately one third of the sugar in water soluble, monomeric form immediately available for fermentation. The bulk of the sugar is tied up in solid lignocellulosic residue and has to be released at additional expense by enzymatic hydrolysis of cellulose. The cost of enzymatic hydrolysis was not included because it is process specific whereas the design goal of the pretreatment process was that it be generic in nature. Some saccharification/fermentation processes will probably have to rely on saccharification of cellulose by separately produced cellulase enzymes. An example of such a process is ethanol production where yeast and bacteria which efficiently ferment sugars to ethanol either do not produce cellulase enzymes at all or if improved by genetic engineering, secrete them in insufficient amounts.

Other potential processes, e.g. anaerobic digestion and single-cell protein production, usually employ cellulolytic microorganisms. The cost of cellulase in these processes is then buried in the overall process costs. Even in the processes relying on the separate production of cellulase enzymes, the rapid evolution of both enzymes and microorganisms producing them makes the estimates of enzyme costs highly inaccurate. In addition, the enzyme loading and saccharification/fermentation times can vary widely according to process configurations and conditions employed. Therefore they have to be investigated and evaluated as a part of the overall bioconversion processes, which are closely coupled to the pretreatment step yet distinct from it.

Table 3 lists the major sections of pretreatment equipment in the process in terms of capital cost and energy consumption. As is apparent, the reactor's installed cost comprises over 35% of the entire plant cost with the knife mill contributing about just under 6%. However, the capital charges are only accountable for 11% of the total cost of production (Table 2); thus improvements in the design of the pretreatment reactor and comminution systems will not improve the economics significantly. The energy consumption of the comminution step is about 92% of the entire plants' energy needs. Therefore, the pretreatment plant is highly vulnerable to the cost of electricity. This vulnerability can be decreased by development of alternate comminution schemes which are less energy intensive than dry milling.

For instance, aspen wood becomes very friable after dilute acid pretreatment, which provides an opportunity for development of additional systems for mechanical disintegration of pretreated chips either before or during enzymatic hydrolysis of cellulose in pretreated biomass. Such developments will have to be coupled to the cheaper design of the pretreatment reactor. The installed cost of the continuous digester made from Carpenter Cb 20-3 is approximately 12 - 18 times higher than the cost of the similar reactor made from carbon steel. The large span in the material costs indicates that the evaluation of cheaper construction materials which retain corrosion resistance at relatively moderate pressures and temperatures would have a great impact on the overall capital cost. The development of different, less expensive reactor configurations which could process wood particles in the size range of 1/8 - 1/2 inch at high concentration of solids would have a similar impact.

While the present study is based on a mild temperature dilute acid pretreatment of biomass, other pretreatment methods such as steam explosion have received a great deal of attention (Iotech, 1982; Wright et al, 1986). Acid processes may have a slight advantage because of their lower operating

temperatures which generate lower quantities of degradation products which may in turn, inhibit downstream processes. Engineering designs prepared to date do not show one method having a major capital or operating cost advantage over another and both pretreatment processes appear to be cost effective.

B. Alkaline Delignification

While dilute acid pretreatment of aspen wood and wheat straw provides highly digestible cellulosic substrate without lignin removal, the downstream processing of pretreated solids by enzymatic saccharification/fermentation to ethanol is somewhat hampered by the presence of lignin. Lignin, which remains quite insoluble in saccharification/fermentation systems forms a sizable (approximately one-third) fraction of the pretreated substrate. This solid fraction has to be carried through saccharification and fermentation as more or less an inert component. The actual substrate, cellulose, is thus diluted and residual lignin also binds cellulose fibers together which creates mixing and comminution problems in saccharification/fermentation sections. In addition, the recent work by us and other investigators indicates that lignin adsorbs some components of cellulase enzyme complex, namely β -glucosidase, thus increasing the enzyme consumption. If lignin is to be used as a cheap boiler fuel, then its presence in the solid form is actually beneficial, because it can be easily recovered at the end of saccharification/fermentation by simple filtration processes, dried and burned. However, such a low value utilization of lignin provides only small economic benefit to the overall process, because another cheap energy source (coal) is replaced by it. Economic studies indicate that upgrading of lignin to higher value liquid fuel additives could create sizable byproduct credits to the overall process.

Separation and recovery of lignin from acid-treated aspen wood and wheat straw can thus have several beneficial effects if marketing of lignin derived products can pay for the increased pretreatment complexity and costs. Dilute sodium hydroxide solutions in water can effectively remove lignin from ligno-cellulosic biomass and with addition of other pulping chemicals, form the basis of major pulp processes today (Sarkanen and Ludwig, 1971). Since the alkaline delignifications are known to proceed more efficiently at elevated temperatures, we have chosen 100°-175°C temperature range for our investigations. We have also performed a limited investigation of pH effects by employing 1, 2, and 4% sodium hydroxide solutions. Aspen wood and wheat straw pretreated with dilute sulfuric acid under two different sets of experimental conditions were used. The first batches were prepared in the 50-gal glass lined reactor by prehydrolysis at 140°C for 1 hour, plus 1 hour each for heat-up and cool-down times. These conditions assure complete hydrolysis of hemicelluloses but may lead to partial hydrolysis of cellulose chains and increased condensation of lignin. The second set of dilute acid pretreatments was performed in a 2-gal stainless steel Parr reactor which can be heated and cooled much faster than the 50-gal reactor. The biomass was pretreated with dilute sulfuric acid at 140°C for 20 minutes, plus five minutes cool-down time. These conditions were selected from our previous kinetic data because they allow nearly complete hydrolysis of xylans (approx. 85 - 90%) and no additional time for hydrolysis of cellulose and condensation of lignin. The conditions which allow incomplete hydrolysis of xylans were not investigated because they would lead to losses and destruction of xylose. The chemical composition of starting materials and acid treated substrates is shown in

Table 4. The substrates and results for both alkaline delignifications and enzymatic digestibility of cellulose are shown in Table 4. and Figures 7 to 15.

The results show that relatively rapid delignification of the substrates occurred under all conditions tested. However, the extent of delignification depends on the substrate, temperature and to the lesser extent on sodium hydroxide concentration. The acid treated wheat straw (Figures 7 and 8) requires much lower temperatures (100 - 120°C) for nearly complete delignifications than acid treated aspen wood which requires temperatures in the range of 140 - 175°C for the same levels of lignin solubilization (Figures 9 and 10). The strength of alkaline solutions also seems to have smaller effects on the lignin solubilization from pretreated wheat straw than from pretreated aspen wood where most concentrated sodium hydroxide solutions (4 wt %) and high temperatures are required for nearly complete lignin removal (Figures 7 to 12). The concentrations of sodium hydroxide tested do not seem to have an effect on solubilization of cellulose from both pretreated substrates (Figures 11 and 12). Increasing temperature initially increases the solubilization of cellulose, but at higher temperatures the effects are very small. The net effect is that solubilization of cellulose levels off before all lignin is removed and the extent of cellulose loss is quite dependent on the substrate and severity of the acid pretreatment. We have not followed destruction of solubilized cellulose at the present time but experience from pulping processes and a single preliminary result indicate that solubilized cellulose is degraded by alkaline peeling reactions.

The different behavior of the two substrates pretreated with dilute acid under two different conditions is best illustrated in Figure 15, where selectivity of lignin removal is plotted against lignin solubilization. The selectivity is defined here as a ratio of lignin removal to solubilization of cellulose. The examination of Figure 15 shows that very high selectivity can be obtained if heat straw is only partially delignified (i.e., approximately 60% of the lignin is solubilized). The selectivity drops rapidly when larger amounts of lignin are being solubilized, which is caused by continuing solubilization of cellulose. The behavior of pretreated aspen wood is entirely different. The selectivity of lignin removal is initially much lower than for wheat straw and it increases slightly as more lignin is removed so at nearly complete delignifications the selectivities for both substrates are similar. This behavior can be explained by rapid initial solubilization of the part of cellulose in pretreated aspen wood and rapid decrease in the rate of its removal as delignification proceeded further.

Milder conditions of dilute acid prehydrolysis have clear beneficial effects in decreasing the solubilization and losses of cellulose, probably by decreasing the hydrolysis of cellulose chains. However, utilization of milder conditions than we used in the second pretreatment set will lead to incomplete hydrolysis of xylans which would then be solubilized and probably destroyed in alkaline delignification step. Therefore, the potential decrease in cellulose losses would be balanced by increasing losses of hemicellulosic sugars and this avenue for increasing selectivity of alkaline delignifications will not be pursued further. The relatively low selectivity of alkaline delignifications of acid treated aspen wood and wheat straw represents the most serious problem of this additional pretreatment at the present time. The cellulose in acid treated substrates is already highly digestible (80 - 100%) by cellulase

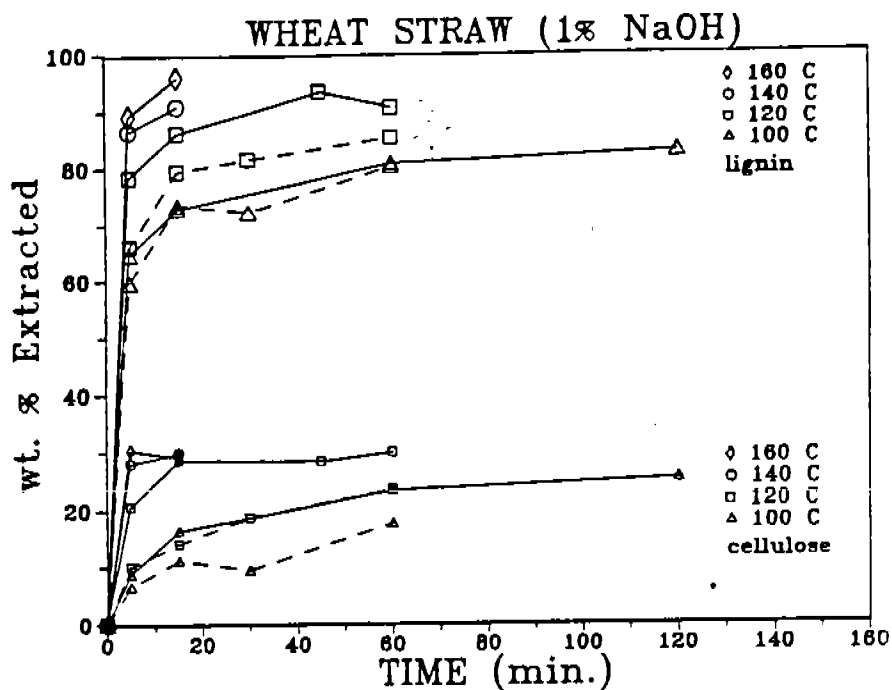


Figure 7. Extraction of lignin and cellulose with 1% sodium hydroxide solution from acid treated wheat straw as a function of time and temperature. The solid lines represent starting substrate pretreated for one hour at 140°C. The dashed lines represent starting substrate pretreated for 20 minutes at 140°C.

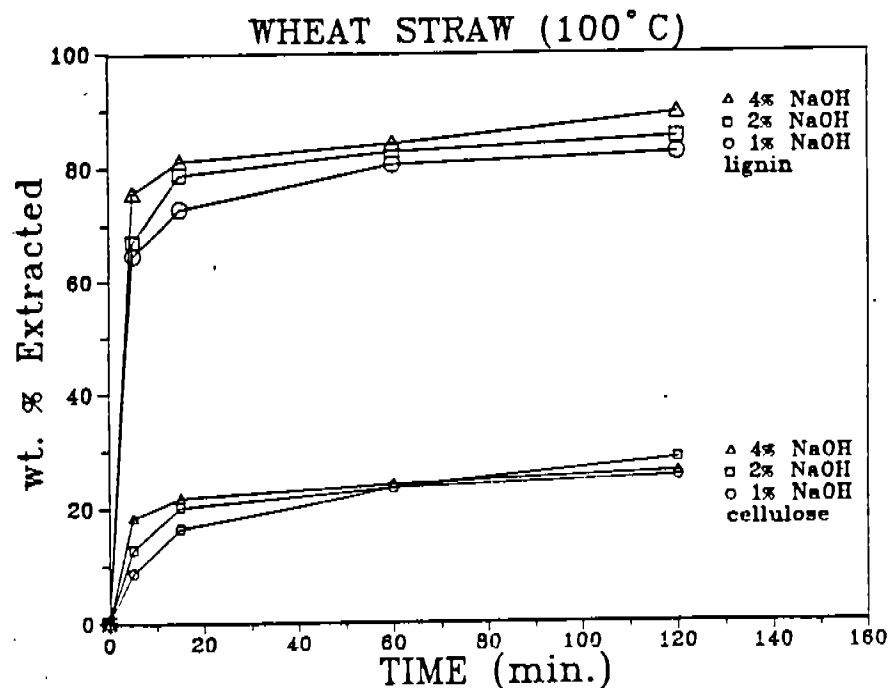


Figure 8. Extraction of lignin and cellulose from acid treated (140°C/one hour) wheat straw at 100°C as a function of time and sodium hydroxide concentration.

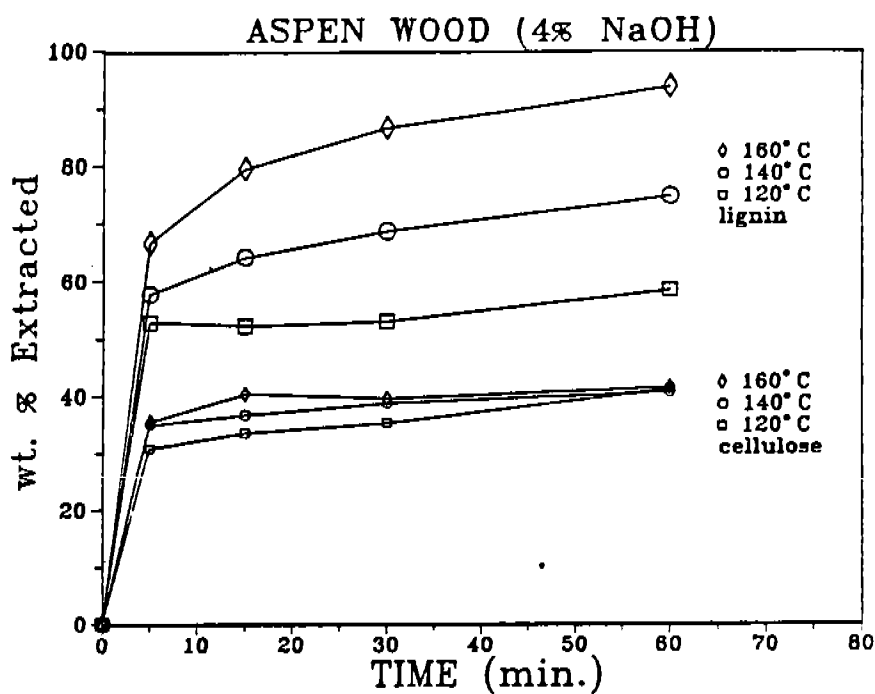


Figure 9. Extraction of lignin and cellulose with 4% sodium hydroxide solution from acid treated aspen wood (140°C/one hour) as a function of time and temperature.

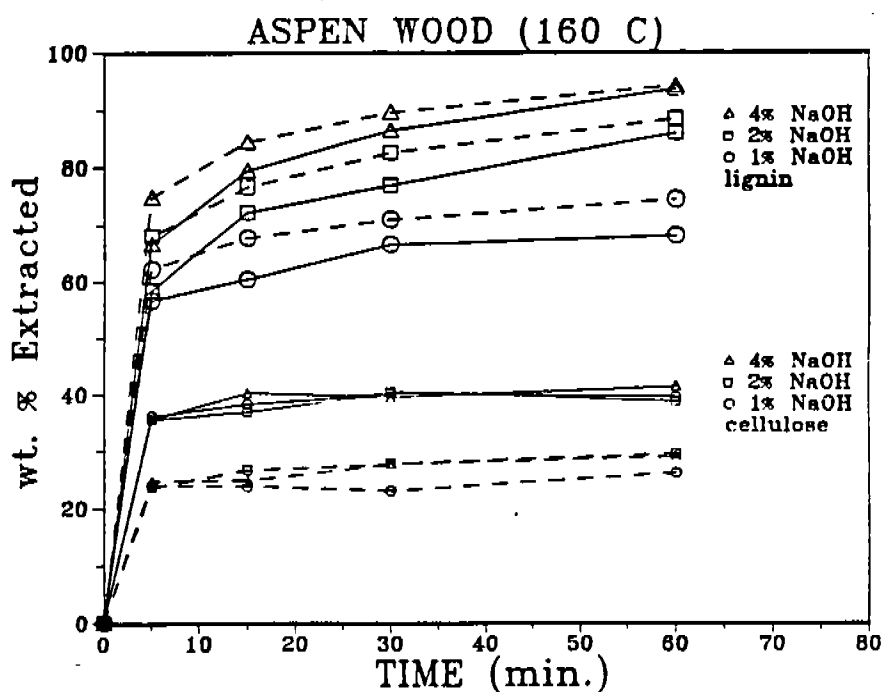


Figure 10. Extraction of lignin and cellulose from acid treated aspen wood at 160°C as a function of time and sodium hydroxide concentration. The solid lines represent starting substrate pretreated for one hour at 140°C. The dashed lines represent starting substrate pretreated for 15 minutes at 140°C.

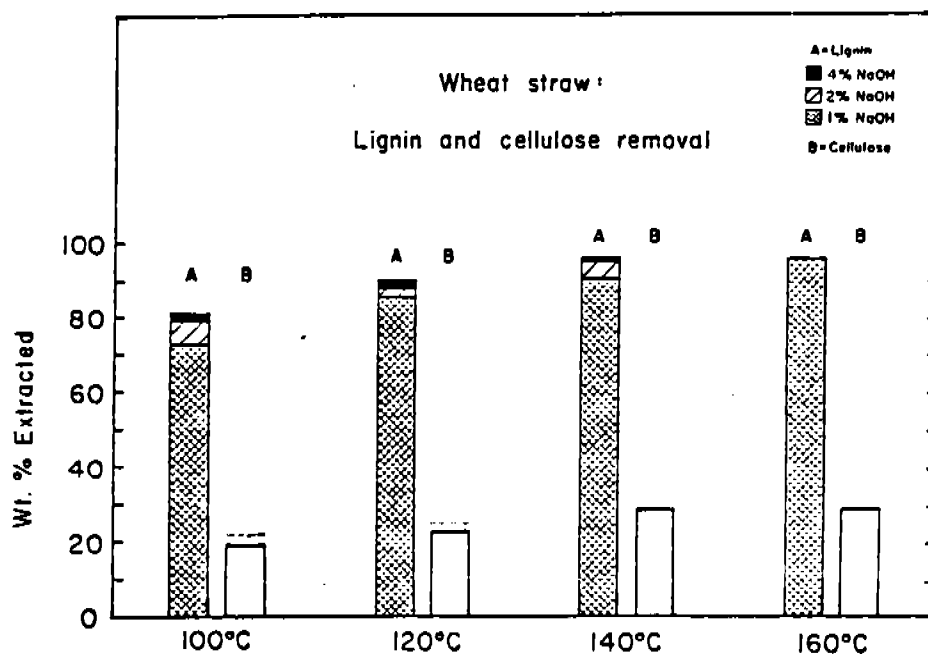


Figure 11. Extraction of lignin and cellulose from acid treated wheat straw (140°C/one hour) as a function of temperature and sodium hydroxide concentration. Reaction time = 15 min.

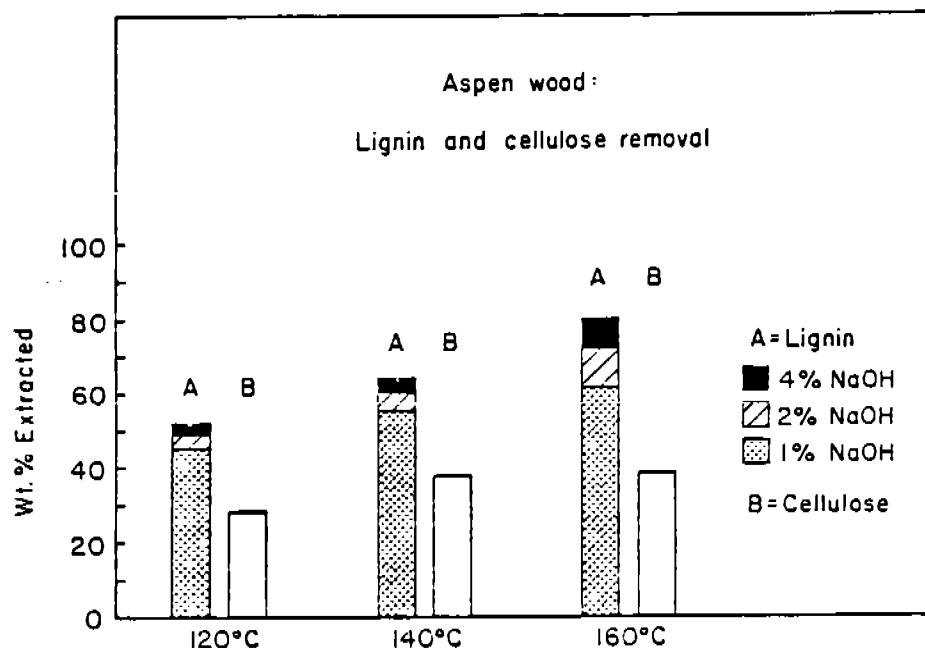


Figure 12. Extraction of lignin and cellulose from acid treated aspen wood (140°C/one hour) as a function of temperature and sodium hydroxide concentration. Reaction time = 15 min.

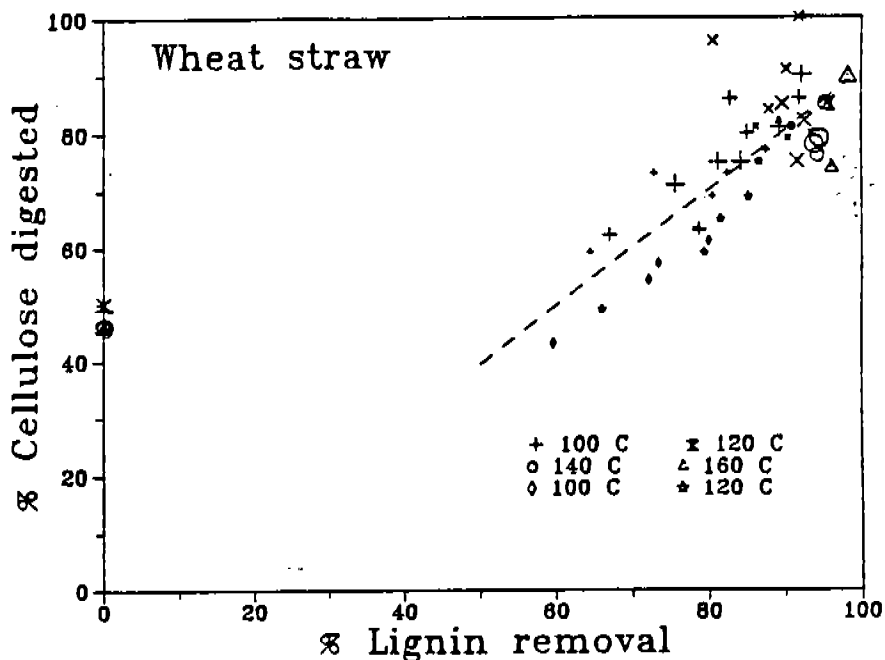


Figure 13. Rapidly digestible fraction of cellulose in alkali-extracted acid treated wheat straw as a function of lignin removal. Reaction time of enzymatic hydrolysis = 7 1/2 hours. The three different sizes of some of the symbols represent the three concentrations of NaOH used, 1%, 2%, and 4%, with the smallest symbol representing 1% and the largest symbol representing 4%. The diamond and the star are data from the 20 minute acid pretreated substrate. All other data are from the one hour pretreated substrate.

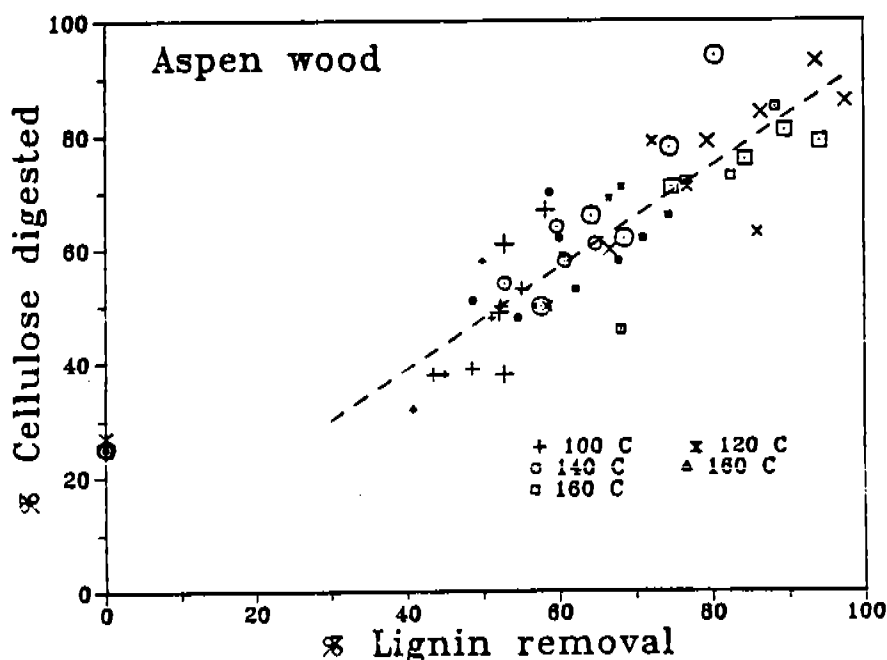


Figure 14. Rapidly digestible fraction of cellulose in alkali extracted acid treated aspen wood as a function of lignin removal. Reaction time of enzymatic hydrolysis = 7 1/2 hours. The three different sizes of the symbols represent the three concentrations of NaOH used, 1%, 2%, and 4%, with the smallest symbol representing 1% and the largest symbol representing 4%. The squares are data from the 20 minute acid pretreated substrate, while all other data are from the one hour pretreated substrate.

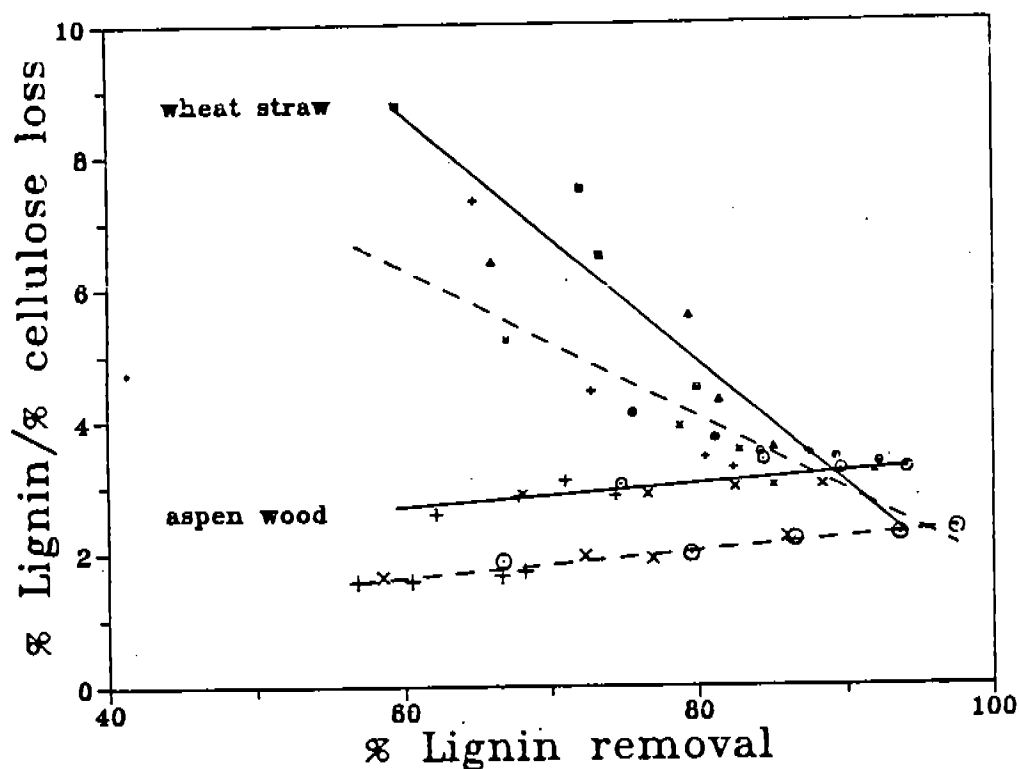


Figure 15. Selectivity of lignin removal as a function of lignin removal for acid treated wheat straw extracted with sodium hydroxide at 100°C (all symbols except triangles on the wheat straw curve) and 120°C (triangle symbols only) and acid treated aspen wood extracted with sodium hydroxide at 160°C. Concentrations of NaOH used were 1% (+, Δ , and \square), 2% (x), and 4% (0). The dashed lines represent data using substrates pretreated for one hour at 140°C. The solid lines represent data from the biomass pretreated at the shorter times at 140°C.

enzyme from Trichoderma reesei so cellulose losses during alkaline delignifications represent a real loss in total sugar yield.

Another, positive, effect of alkaline delignification has been observed. The rate of cellulose hydrolysis increases dramatically with the severity of alkaline delignifications. Increasing amounts of cellulose can be rapidly digested (i.e., in 7.5 hours) as increasing amounts of lignin are being removed (Figures 13 and 14). High levels of cellulose hydrolysis take approximately 72 - 96 hours for acid treated aspen wood and wheat straw and approximately the same time for cellulose controls (i.e., α -cellulose, Solka Floc and Sigmacell-50) using the same enzyme loading as for alkali treated materials. This large increase in the rate of cellulose digestion would have a tremendous positive impact on sections downstream in the enzymatic saccharification/fermentation step. A similar observation about positive effects of alkaline treatments on digestibility of cellulose have been made by Austrian researchers (Schurz, 1986), but neither they nor we can provide clear rationale for these observations. The concentrations of sodium hydroxide we have employed are too low for transition from cellulose I to cellulose II to occur (Purz and Fink, 1983). The increase in cellulose digestibility correlates quite well with removal of lignin (Figures 13 and 14). It does not seem to correlate with solubilization of cellulose (data not shown) but in this case the relationships can be obscured by the fact that solubilization of cellulose seems to level off well before the substrates are delignified. The simplest explanation for our observations is the increase in surface area of cellulose fibers accessible to cellulase enzymes due to removal of undigestible encrusting substances (lignin). The experimental characterization of alkali treated aspen and wheat straw substrates is planned to shed light on underlying mechanisms of observed pretreatment effects.

C. Dilute Acid Pretreatment of Aspen Bark

The pretreatment experiments were initiated, however, problems were encountered with analytical methods and results. Therefore, we cannot report experimental results at the present time.

Future Thrusts

Calendar Year 1987. The alkaline delignifications of acid treated aspen wood and wheat straw will be extended to solutions of sodium hydroxide in alcohol (i.e., methanol and ethanol), water mixtures. The addition of lower alcohols is known to suppress solubilization of carbohydrates and therefore it should increase selectivity of delignification. The characterization of alkali treated aspen wood and wheat straw will be initiated. The experimental efforts in alkaline delignifications will be suspended by the end of CY1987.

The dilute acid pretreatment of aspen bark will be completed and results evaluated.

Calendar Year 1988. Characterization of acid and alkali treated aspen wood and wheat straw will be completed.

Preliminary investigations of dilute acid pretreatment of four hardwood species and three herbaceous plant species, selected and provided by biomass production program at Oak Ridge National Laboratory, will be completed.

Pretreatment of wood, bark, and wood with bark will be evaluated and results provided to ORNL as a feedback for production of short-rotation, woody, and herbaceous plant crops.

Pretreated substrates will be provided for experiments in simultaneous saccharification/fermentation of cellulose to ethanol.

Investigation of methods for disintegration of wet, pretreated aspen wood either before or during enzymatic saccharification will be initiated.

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EFFECT OF NON-UNIFORM TEMPERATURE DISTRIBUTION
ON ACID HYDROLYSIS OF ASPEN HEMICELLULOSE

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ABSTRACT

The thermal diffusivities of Aspen wood were experimentally determined. The data were incorporated into a theoretical model designed to study the effect of transient temperature variation within the solid substrate during acid catalyzed hydrolysis of hemicellulose (prehydrolysis). The kinetic and the modelling results were analyzed to assess the effect of particle size on acid hydrolysis of hemicellulose. Among the important findings was that as the chip size increases, the maximum attainable yield of xylose decreases and the reaction time at which the maximum yield occurs increases. This effect becomes more significant as the temperature and the acid level increases. Quantitative criteria were therefore established to show the effect of particle size on the yield and the reaction time at various reaction conditions.